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[11] The significant absorption observed at 353 nm should not be confused with the overall maximum in the UV absorption spectrum, which typically occurs below 300 nm in thermotropic LCs. Our comments are based on detailed measurement of the polarized absorption spectra from 200 to 800 nm.

Organization of Bridging Organics in Periodic Mesoporous Organosilicas (PMOs)—Polarization Micro-Raman Spectroscopy**

By *Ömer Dag* and *Geoffrey A. Ozin**

Periodic mesoporous organosilicas (PMOs) with bridging organic groups as an integral portion of the silica framework are an exciting new class of hybrid materials, in which the interface between the silica and organic constituents is under molecular scale control.[1,2] These novel nanocomposites of organic and inorganic parts are synthesized by a "bottom-up" materials chemistry approach rather than by "top-down" engineering materials methods. The ultimate goal is the same—the integration of inorganic and organic components to create a new material whose properties are distinct from the sum of its parts. The synthesis of PMOs is based on the hydrolytic polycondensation of an alkoxysilane with bridging organic groups $[(R'O)_3Si]_nR$ located in the microphase-separated domains of a lyotropic liquid crystal template. In essence, the structure of the templating mesophase is "petrified" as a skin of polymerized organosilicate.

The pure silica archetype of the PMOs is periodic mesoporous silica, MCM-41.[3] This material is formed using the precursor $(EtO)_4Si$. In this case, the surfactant templating mesophase is imbibed within the void spaces of the periodic mesoporous silica product. Removal of the surfactant by solvent extraction, ion-exchange or calcination and its subsequent replacement, through host–guest inclusion chemistry, by an organic[4] or inorganic[5] polymer, yields a periodic mesostructured silica–polymer nanocomposite material, which can subsequently be transformed to a periodic mesostructured silica–ceramic hybrid.[5] The use of a mononuclear alkoxysilane precursor, $(EtO)_3SiR$, in the self-assembly surfactant-based synthesis leads to an organic functionalized mesoporous silica hybrid material, in which organic groups are terminally bonded to the silica walls and suspended within the channel space.[6] Mesoporous organosilicas of this genre enable "chemistry in the channels" and facilitate the development of "smart nanocomposites" that can function, for example, as a heavy metal sponge, a nacre mimic or a chiral separation stationary phase.[7,8]

Binuclear alkoxysilane precursors, $(EtO)_3Si–R–Si(OEt)_3$, allow the assembly of periodic mesoporous organosilica nanocomposite materials with bridge-bonded organic groups housed "inside" the channel walls.[1,2] These PMOs facilitate "chemistry of the channels" and provide new opportunities for controlling the chemical, physical, mechanical, and dielectric properties of the materials.[1,2] PMOs are distinct from organosilica xerogels, which are synthesized by the hydrolytic polycondensation of an alkoxysilane in the absence of a surfactant-template.[9] This lack of structure control results in an a-periodic material with a chaotic arrangement of polydispersed mesopores.

Recently we described the co-assembly of $(EtO)_3Si–R–Si(OEt)_3$ precursors with a non-ionic $C_{12}H_{25}(EO)_{10}H$ lyotropic liquid crystal template, to form PMOs in the form of an oriented film, oriented periodic mesoporous organosilica film (OPMOF).[2] The bridging organics were R = ethane, ethene, thiophene, and benzene homogeneously integrated into the silica framework. A multi-technique diffraction, microscopy, and spectroscopy approach to the characterization of OPMOF provided valuable structural information about the crystalline mesoporosity of OPMOF; however, the methods used lacked the ability to provide molecular scale information concerning the "spatial organization" of the bridge bonded organics within the silica channel walls. Although the distribution of bridge-bonded organics in the silica framework is homogeneous, their orientation with respect to the channel director field is unknown.

Herein we demonstrate that polarization micro-Raman spectroscopy (PMRS) in conjunction with powder X-ray diffraction (PXRD) and polarization optical microscopy (POM) is uniquely able to address the interesting issue of how bridge-bonded organic groups are organized within the silica channel walls of OPMOF. Specifically, the anisotropy of Raman scattering can be used to distinguish a glassy microstructure from an ordered one for the organic moieties distributed within the organosilica channel walls of OPMOF.

The synthesis and structural characterization of hexagonal symmetry OPMOF containing bridge-bonded ethane, ethene, thiophene, and benzene groups dispersed homogeneously inside the silica channel walls have been described.[2] To amplify on key structural details of OPMOF in order to appreci-

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ate the results of the present study, PXRD measurements demonstrate that the mesoscale channels run parallel to the surface of the underlying glass substrate used to grow the film. Transmission electron microscopy (TEM) images of microtomed sections of OPMOF confirm the channels are aligned parallel to the surface of the OPMOF as is the case for hexagonal periodic mesoporous silica grown as a film on glass as well as other substrates such as mica and graphite.[10,11] TEM images recorded over large areas of the film show that the material is homogeneous—a mesoporous organosilica with structure based on a periodic array of monodispersed mesopores with no evidence of an organosilica xerogel phase with randomly and broadly distributed mesopores. POM images of OPMOF recorded between crossed polarizers, display an optical birefringence pattern with a fan-texture over the entire area of the film that is characteristic of a hexagonal mesoporous organosilica with the channels organized in the plane of the film Figure 1. This is just like that found for periodic mesoporous silica film.[10,11] Multinuclear (^{1}H, ^{13}C, ^{29}Si) cross

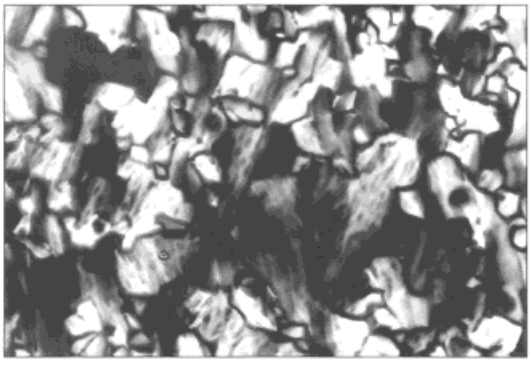

Fig. 1. Polarized optical microscopy (POM) image of oriented mesoporous thiophenesilica film showing the optical birefringence fan-texture of the hexagonal phase.

polarization magic angle spinning nuclear magnetic resonance (CP MAS NMR) and Fourier transform Raman (FTR) spectroscopy define the presence of the bridge-bonded organic groups in the silica framework with negligible hydrolytic cleavage of the silicon–carbon bond.

PMRS is an interesting technique for interrogating with spatial resolution, at the optical length scale, anisotropy of vibrational modes in hexagonal symmetry OPMOF. As mentioned above PXRD and POM show that the channel director field meanders in the plane of the film—it swirls and curls around topological line-disclination defects.[10,11] Raman polarization measurements on OPMOF with the electric vector of the incident and scattered laser light along specified directions of the film can therefore be used to distinguish a preferred orientation from a random distribution of bridge-bonded organic groups housed inside the silica channel walls.

To amplify, the ability to record spatially selected area submicrometer scale PMRS from different regions of the OPMOF allows one to probe the orientation of bridge-bonded organic groups inside the channel walls by observation of the polarization anisotropy of fingerprint vibrations. This is possible because the spatial extent of line disclinations in OPMOF is at least an order of magnitude larger in size than the area interrogated by the laser Raman probe beam, Figure 1. Thus PMRS can provide structural information about straight channel regions of OPMOF. It is important to note that both micro-Raman spectra and TEM images recorded over large areas of OPMOF are identical, thereby defining compositional and structural homogeneity of OPMOF.

A representative set of $\parallel/\parallel$ and $\parallel/\perp$ PMRS are shown for hexagonal OPMOF containing bridge-bonded ethane, ethene, thiophene, and benzene groups housed inside the silica channel walls, Figure 2. Diagnostic non-ionic surfactant and bridge-bonded organic fingerprint modes of OPMOF are identified by comparison with the PMRS of a control sample, oriented mesoporous silica film, which contained the surfactant template but is devoid of the bridge-bonded organic moiety, Table 1. Inspection of the Raman spectra of OPMOF immediately reveals two categories of polarization behavior for the vibrational modes of the framework organics—those that are strongly "polarized" in parallel $\parallel/\parallel$ and $\perp/\perp$ and those that are essentially "depolarized" in crossed $\parallel/\perp$ and $\perp/\parallel$ measurements.

To expand, the strongly polarized band that occurs in the range ca. 510–630 cm^{-1} for OPMOF containing ethane, ethene, thiophene, and benzene groups flags the totally symmetrical νSi–C stretching motion associated with the bridge-bonded organic groups inside the silica channel wall. The breadth and structure of this band likely originates from C–SiO$_n$(OH)$_{3-n}$, T_n sites (n = 0–3) that have previously been observed by ^{13}C, ^{29}Si MAS NMR spectroscopy. Other strongly polarized Raman bands associated with the organic moiety are ascribed to symmetrical νC=C stretching of ethene, νC–S stretching of thiophene, and various δC–H ring deformations. Depolarized Raman bands are ascribed to asymmetric stretching and bending modes, of the organic moiety housed inside the silica channel wall, Table 1. Note that powdered samples of OPMOF display no polarization effects in their micro-Raman spectra. This is because the incident and scattered light suffers multiple internal reflections in the randomly oriented PMO particles, which causes birefringence depolarization of the Raman spectra of powdered OPMOF.

The polarization behavior of OPMOF with ethane, ethene, thiophene, and benzene functionality is remarkably consistent in that one "never" observes enhanced Raman intensity in any crossed polarization measurements. This would be expected for bridge-bonded organic groups that have a principal molecular axis oriented in some way with respect to the channel director field. These observations imply that the bridging organic groups are not behaving as if they are preferentially aligned with respect to the director field of the silica channels. Instead the organics appear to be randomly organized within the silica walls—the observed PMRS are diagnostic of a glassy organosilica. In other words, the material is behaving like an "oriented gas" with respect to the organic

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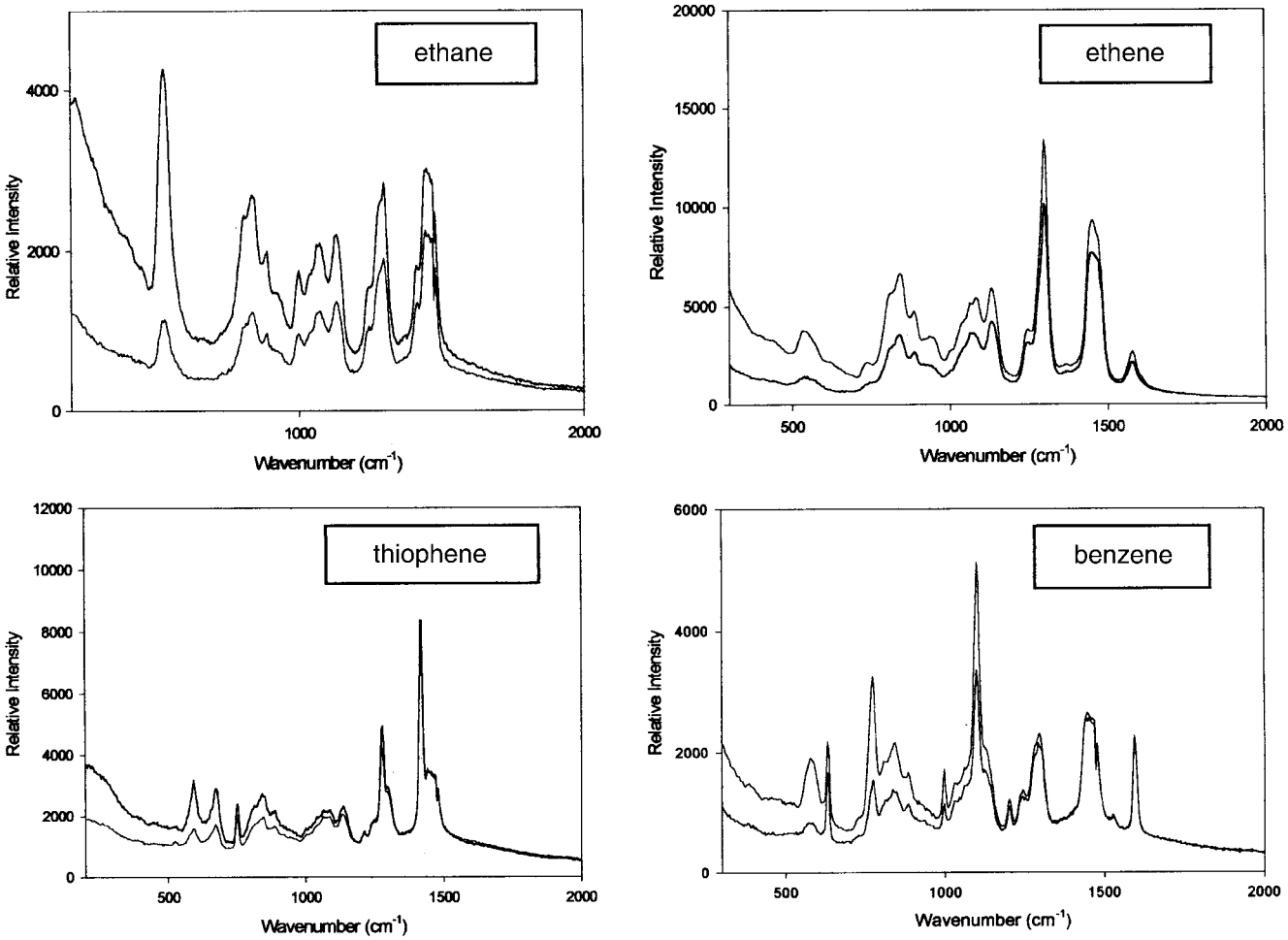

Fig. 2. PMRS showing ∥/∥ and ∥/⊥ polarization data for oriented film samples of (top left) hexagonal mesoporous ethanesilica, (top right) hexagonal mesoporous ethenesilica, (bottom left) hexagonal mesoporous thiophenesilica, and (bottom right) hexagonal mesoporous benzenesilica.

moieties where an isotropic arrangement of bridge-bonded organic groups are "frozen" inside the channel walls of oriented hexagonal mesoporous organosilica film. The absence of high angle PXRD reflections in OPMOF and powdered OPMOF is consistent with the proposal that the microstructure of the organosilica walls is glassy.

Interestingly, oriented PMO film with bridging ethane and ethene groups templated by the cationic surfactant cetyltrimethylammonium bromide $(C_{16}H_{33}N(CH_3)_3)^+Br^-$ display in PRMS enhanced Raman intensity for some of the surfactant modes, implying the cationic surfactant molecules/micelles are well ordered in the channels in contrast to the non-ionic ones, Table 1. This is to be expected because under acidic synthesis conditions electrostatic interactions between the cationic surfactants/micelles, anions and protonated organosilicates control the assembly of the organosilicatropic mesophase in an analogous way to the purely silicatropic mesophase in hexagonal mesoporous silica preparations.[10,11] On polymerization of the organosilicatropic mesophase to form the PMO, it is these electrostatic interactions that serve to organize the cationic surfactants/micelles with respect to the anionic silica framework, a situation less likely for non-ionic surfactants.

PMRS measurements of oriented periodic mesoporous organosilica film indicate that the best description of the structure at the mesoscale and microscale is a hexagonal array of channels with glassy organosilica walls. This is analogous to the glassy silica microstructure of the channel walls found for hexagonal mesoporous silica, MCM-41.[3]

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Table 1. PRMS results for OPMOF with bridge bonded ethane (BTA), ethene (BTE), thiophene (BTT), and benzene (BTB) groups "inside" the channel walls [a].

Band frequency [cm^{-1}]	Polarization ratio [b]	Vibrational assignment
Hexagonal mesoporous ethanesilica, BTA [d]		
1441, 1468	0.75	δ CH_2 $C_{12}H_{25}(EO)_{10}H$ tail
1411	0.84	δ CH_2 BTA
1132	0.67	ν C-O-C $C_{12}H_{25}(EO)_{10}H$ head
513, 531, 560	0.23	ν Si-C [c]
Hexagonal mesoporous ethenesilica, BTE [d]		
1575	0.74	ν C=C BTE
1443, 1470	0.84	δ CH_2 $C_{12}H_{25}(EO)_{10}H$ tail
1133	0.58	ν C-O-C $C_{12}H_{25}(EO)_{10}H$ head
1000	0.39	δ CH BTE
942	0.34	δ CH BTE
808	0.35	δ CH BTE
527, 543, 572	0.31	ν Si-C [c]
Hexagonal mesoporous thiophenesilica, BTT [d]		
1441, 1468	1.00	δ CH_2 $C_{12}H_{25}(EO)_{10}H$ tail
1417	0.80	BTT (ring stretching)
1277	0.79	δ CH BTT (in plane)
1132	0.74	ν C-O-C $C_{12}H_{25}(EO)_{10}H$ head
752	0.75	δ CH BTT (out of plane)
674	0.43	ν C-S BTT
574, 595, 630	0.33	ν Si-C [c]
Hexagonal mesoporous benzenesilica, BTB [d]		
1596	1.00	ν C-C BTB (ring stretch)
1442, 1468	1.00	δ CH_2 $C_{12}H_{25}(EO)_{10}H$ tail
1132	0.87	ν C-O-C $C_{12}H_{25}(EO)_{10}H$ head
1101	0.55	δ CH BTB (in-plane)
997	0.84	BTB (ring breathing)
773	0.43	BTB (ring vibration)
633	1.00	δ CH BTB (out of plane)
561, 582, 617	0.33	ν Si-C [c]
Hexagonal mesoporous ethenesilica, BTE [e]		
1578	0.35	ν C=C BTE
1443, 1457	1.10	δ CH_2 $C_{16}H_{33}N(CH_3)_3^+$
1305	0.90	Surfactant
970	1.60	Surfactant
910	1.19	Surfactant
763	0.42	Surfactant
527, 543, 572	0.34	ν Si-C [c]
Hexagonal mesoporous ethanesilica, BTA [e]		
1450	1.35	δ CH_2 $C_{16}H_{33}N(CH_3)_3^+$
1420	1.40	δ CH_2 $C_{16}H_{33}N(CH_3)_3^+$
1410	0.61	δ CH_2 BTA
1305	1.16	Surfactant
1037	1.31	Surfactant
763	0.20	Surfactant
513, 531, 560	0.08	ν Si-C [c]

[a] PRMS results were obtained on a Instruments S. A. LabRam Raman microscope. The Raman signal was collected over a spatial area of roughly 2 μm × 2 μm and the collection optics for Raman scattered light were configured in a 180° geometry. Wavelengths and polarization ratios were calibrated against carbon tetrachloride. [b] Polarization ratio is $I(\|/\perp)/I(\|/\|)$. [c] Assigned to C–$SiO_n(OH)_{3-n}$, T_n sites, where n = 0–3 (see text). [d] Non-ionic surfactant template. [e] Cationic surfactant template.

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Macrocrystalline Colloidal Assemblies in an Electric Field**

By *Gi-Ra Yi*, *Jun Hyuk Moon*, and *Seung-Man Yang**

Colloidal particles are interesting and versatile building block for two- and three-dimensional microstructures.[1] Because of their nearly monodisperse nature, colloidal particles can self-assemble into long-range lattices when appropriately settled or dried out of their supporting solvent. Well-controlled colloidal assemblies display a number of potentially applicable characteristics such as a photonic bandgap,[2] high packing density, and high surface-to-volume ratio. For practical applications of these structures, they should be mounted or shaped into usable objects.[3] To address this problem, a number of methods have been exploited using colloidal crystallization in confined geometry, including gravity sedimentation on flat or periodically patterned substrates, flow of the colloids through micromachined channels or a smooth narrow pore membrane, and making use of capillary forces.[4] One of the simplest approaches involves the use of a "suspension droplet" as a confined geometry (i.e., a liquid droplet containing a number of colloidal particles inside). When the suspension droplet is dried, the crystallization of submicrometer-sized colloidal particles occurs inside the droplet, leading to a highly ordered colloidal assembly.[5] Such structured materials have important applications to photonic crystals,[6] size-exclusion chromatography,[7] electronic paper in the case of magnetic and color anisotropic particles,[8] and electrorheological or magnetorheological fluids. Meanwhile, for practical applications, microstructured bodies of non-spherical shape may be of considerable significance.[9] In the previous works of

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